



- (51) **International Patent Classification:**
C08G 59/42 (2006.01) *C08J 5/24* (2006.01)
- (21) **International Application Number:**
PCT/US2014/062615
- (22) **International Filing Date:**
28 October 2014 (28.10.2014)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
PCT/CN2013/086378
31 October 2013 (31.10.2013) CN
- (71) **Applicant:** **DOW GLOBAL TECHNOLOGIES LLC**
[US/US]; 2040 Dow Center, Midland, MI 48674 (US).
- (72) **Inventors:** **ZHANG, Chao**; Room 301, Building 7, No. 828 Bei'ai Road, Shanghai, 200125 (CN). **FENG, Yanli**; Room 502, Building 66, No. 300 Chuangxinxi Road, Baolijinjue, Tangzhen, Pudong District, Shanghai, 201203 (CN). **CHEN, Hongyu**; Guanglan Road, Lane 50, No. 57, Room 102, Zhangjiang, Shanghai, 201203 (CN). **MULLINS, Michael J.**; 2217 Sheridan Street, Houston, TX 77030 (US). **ZHANG, Yi**; Room 1A, No. 32, Lane 999, Changshou Road, Jingan District, Shanghai, 200042 (CN). **XIONG, Jiawen**; Room 301, Building 92, Lane 3339, Shangnan Road, Pudong New District, Shanghai, 200126 (CN). **FANG, Lijing**; Room 2D, Building Yongxiangju No. 28, Xiangxuan Road, Futian District, Shenzhen, 518040 (CN). **LIAO, Guihong**; Room 602, No. 1 Building

10, Lane 171, Jianzhong Road, Pudong District, Shanghai, 201210 (CN).

- (74) **Agent:** **WELVAERT, Bronwyn**; The Dow Chemical Company, P.O. Box 1967, Midland, Michigan 48641-1967 (US).

(81) **Designated States** (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) **Title:** CURABLE COMPOSITIONS WHICH FORM INTERPENETRATING POLYMER NETWORKS

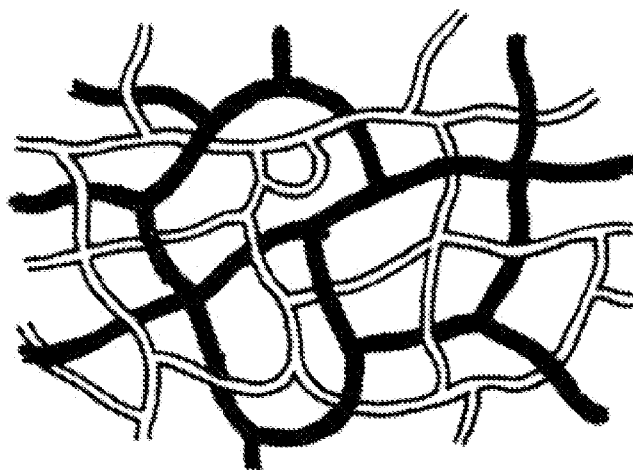


FIGURE 1

(57) **Abstract:** A curable composition comprising a) an epoxy component; b) a hardener component selected from the group consisting of a maleic anhydride-containing compound, a maleic anhydride-containing vinyl compound, and combinations thereof; and c) a vinyl component wherein upon curing under curing conditions, the curable composition forms at least one interpenetrating polymer network is disclosed.

CURABLE COMPOSITIONS WHICH FORM INTERPENETRATING POLYMER NETWORKS

Field of Disclosure

5 Embodiments of the present disclosure relate to curable compositions and in particular to curable compositions that include polymers that form interpenetrating polymer networks upon curing.

Background

10 Curable compositions are compositions that include thermosettable monomers that are able to be crosslinked. Crosslinking, also referred to as curing, converts curable compositions into crosslinked polymers (i.e., a cured product) useful in various fields such as, for example, composites, electrical laminates and coatings. Some properties of curable compositions and crosslinked polymers that can be
15 considered for particular applications include mechanical properties, thermal properties, electrical properties, optical properties, processing properties, among other physical properties.

Curable compositions can be cured to form an interpenetrating polymer network (IPN), which is depicted in Figure 1. An IPN is a combination of two or more
20 polymers that form networks wherein at least one polymer is polymerized and/or crosslinked as a network in the presence of the other polymers. Systems that can be dually cured are useful for forming an IPN.

Glass transition temperature, dielectric constant and dissipation factor are examples of properties that are considered as highly relevant for curable compositions
25 used in electrical laminates. For example, having a sufficiently high glass transition temperature for an electrical laminate can be very important in allowing the electrical laminate to be effectively used in assembly processes and service environments to resist working temperature. Similarly, decreasing the dielectric constant (Dk) and dissipation factor (Df) of the electrical laminate can assist in minimizing signal loss in
30 high speed transmissions.

It is well known that vinyl systems tend to have low Dk and Df values, but due to the lack of polar groups, they also tend to have low peel strength with copper and low bonding strength to glass fiber. Meanwhile, resins comprising an epoxy composition and a hardener generally have good adhesion to either copper or glass fiber, but tend to have higher Dk and Df values after curing, due to polar groups present after curing. Maleated polybutadiene (LPBMA) is a multifunctional vinyl that can also be used as an epoxy hardener. However, epoxy resins cured with LPBMA have lower glass transition temperatures (Tg). Therefore, an affordable electrical laminate with a desired balance of thermal properties, adhesion properties and electrical properties would be beneficial.

Brief Description of the Figure

Figure 1 depicts an interpenetrating polymer network structure.

15 Summary

One broad aspect of the present invention discloses a curable composition comprising, consisting of, or consisting essentially of a) an epoxy component; b) a hardener component selected from the group consisting of a maleic anhydride-containing compound, a maleic anhydride-containing vinyl compound, and combinations thereof; and c) a vinyl component and wherein, upon curing under curing conditions, the curable composition forms at least one interpenetrating polymer network.

Detailed Description

25 Epoxy Component

The present invention curable composition includes at least one epoxy resin. The epoxy resin may be saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic and may be substituted. The epoxy resin may also be monomeric or polymeric.

30 The epoxy resins may vary and can include conventional and commercially available epoxy resins, which may be used alone or in combinations of two or more.

In choosing epoxy resins for compositions disclosed herein, consideration should not only be given to properties of the final product, but also to viscosity and other properties that may influence the processing of the resin composition.

Particularly suitable epoxy resins known to the skilled worker are based on reaction products of polyfunctional alcohols, phenols, cycloaliphatic carboxylic acids, aromatic amines, or aminophenols with epichlorohydrin. A few non-limiting embodiments include, for example, bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, resorcinol diglycidyl ether, and triglycidyl ethers of para-aminophenols. Other suitable epoxy resins known to the skilled worker include reaction products of epichlorohydrin with o-cresol and, respectively, phenol novolacs. Further epoxy resins include epoxides of divinylbenzene or divinylanthracene. It is also possible to use a mixture of two or more epoxy resins.

The epoxy resins useful in the present invention may be selected from commercially available products; for example, D.E.N.® ('DEN') 425, DEN 438, DEN 439, D.E.R.® ('DER') 332, DER 331, DER 383, DER 530, DER 538, DER 542, DER 560, DER 592, and DER 593, epoxy resins available from The Dow Chemical Company, and mixtures of any two or more thereof.

For one or more embodiments, the curable composition comprises a multifunctional epoxy resin. In various embodiments, the multifunctional epoxy resin is present in the epoxy component in the range of from 0 weight percent to 100 weight percent, is present in the range of from 0 weight percent to 60 weight percent in various other embodiments, and is present in the range of from 0 weight percent to 50 weight percent in yet various other embodiments, based on the total weight of the epoxy component.

In various embodiments, the epoxy component can comprise a flame retardant epoxy resin. Examples of epoxy resins with flame retardant compounds include, but are not limited to aliphatic epoxy resins, cycloaliphatic epoxy resins, bisphenol A epoxy resins, bisphenol F epoxy resins, phenol novolac epoxy resins, cresol-novolac epoxy resins, biphenyl epoxy resins, polyfunctional epoxy resins, naphthalene epoxy resins, divinylbenzene dioxide, 2-glycidylphenylglycidyl ether, dicyclopentadiene-

type epoxy resins, phosphorous containing epoxy resins, multi aromatic resin type epoxy resins, and mixtures of any two or more thereof.

Hardener

5 For one or more embodiments, the curable composition comprises a polymeric anhydride hardener. Generally, the hardener is selected from the group consisting of a maleic anhydride-containing compound, a maleic anhydride-containing vinyl compound, and combinations thereof. In various embodiments, the polymeric anhydride is a maleic anhydride. In various embodiments, the hardener component
10 can be formed by the copolymerization of a vinyl-containing compound and a maleic anhydride.

Examples of the hardener can include, but are not limited to polybutadiene co-maleic anhydride, styrene-maleic anhydride, maleinized polybutadiene styrene copolymer, and combinations thereof. Specific examples include, but are not limited
15 to (SMA) or maleinized polybutadiene styrene copolymer (SBMA), maleated polybutadiene (LPBMA) and mixtures of any two or more thereof.

The epoxy component and hardener component are together generally present in the curable composition in an amount in the range of from 0.1 weight percent to 99.9 weight percent, based on the total weight of the curable composition. In another
20 embodiment, the epoxy component and hardener component are present together in an amount in the range of from 0.1 weight percent to 60 weight percent.

Vinyl Component

In one or more embodiments, the curable composition contains a vinyl
25 component. In various embodiments, the vinyl component has a number average molecular weight in the range of from 80 to 10000 and is in the range of from 1000 to 2000 in various other embodiments. In various embodiments, the vinyl component comprises vinyl groups that are reactive with epoxide groups. Examples of vinyl components that can be used include, but are not limited to vinyl capped
30 poly(phenylene ether) (vinyl PPO), 1,3,5-triallyl isocyanurate (TAIC), divinylbenzene

(DVB), dicyclopentadiene (DCPD), vinyl capped tetrabromobisphenol A (VTBBA), vinyl capped bisphenol A, vinyl capped phenol novolac, vinyl capped naphthol novolac (VNPN), bismaleimide, maleated rosin, and mixtures of any two or more thereof.

In an embodiment, the vinyl component is present in an amount in the range of from 0.1 weight percent to 99.9 weight percent, based on the total weight of the curable composition. The vinyl component is present in the curable composition in the range of from 0.1 weight percent to 50 weight percent in another embodiment, and is present in the range of from 0.1 weight percent to 40 weight percent in yet another embodiment.

Optional Components

In one or more embodiments, the curable composition can also include an initiator for free radical curing. Examples of such free radical initiators include, but are not limited to dialkyldiazenes (AIBN), 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, diaryl peroxides such as benzoyl peroxide (BPO), dicumyl peroxide (DCP), disulfides, and mixtures thereof.

The free radical initiator is generally present in the curable composition in an amount in the range of from 0.01 weight percent to 10 weight percent, based on the total weight of the curable composition. In another embodiment, the free radical initiator is present in an amount in the range of from 0.1 weight percent to 8 weight percent, and is present in an amount in the range of from 2 weight percent to 5 weight percent in yet another embodiment.

Optionally, catalysts can be added to the curable composition. Examples of catalysts that can be used include, but are not limited to 2-methyl imidazole (2MI), 2-phenyl imidazole (2PI), 2-ethyl-4-methyl imidazole (2E4MI), 1-benzyl-2-phenylimidazole (1B2PZ), boric acid, triphenylphosphine (TPP), tetraphenylphosphonium-tetraphenylborate (TPP-k) and mixtures thereof.

The catalyst is generally present in the curable composition in an amount in the range of from 0.01 weight percent to 20 weight percent, based on the total weight of the curable composition. In another embodiment, the catalyst is present in an amount in the range of from 0.05 weight percent to 10 weight percent, and is present

in an amount in the range of from 0.02 weight percent to 3 weight percent in yet another embodiment.

In one or more embodiments, the curable composition can also include additional flame retardants. Examples of flame retardants include halogen containing compounds, such as, for example, brominated polyphenols such as tetrabromobisphenol A (TBBA) and tetrabromobisphenol F and materials derived therefrom: TBBA-diglycidyl ether, reaction products of bisphenol A or TBBA with TBBA-diglycidyl ether, and reaction products of bisphenol A diglycidyl ether with TBBA. In various embodiments, a composition that does not contain halogen can be used, such as, for example phosphorus-containing compounds. Examples of phosphorus-containing compounds that can be used include but are not limited to HCA, dimethylphosphite, diphenylphosphite, ethylphosphonic acid, diethylphosphinic acid, methyl ethylphosphinic acid, phenyl phosphonic acid, vinyl phosphonic acid, phenolic (HCA-HQ); tris(4-hydroxyphenyl)phosphine oxide, bis(2-hydroxyphenyl)phenylphosphine oxide, bis(2-hydroxyphenyl)phenylphosphinate, tris(2-hydroxy-5-methylphenyl)phosphine oxide, M-acid-AH, bis(4-aminophenyl)phenylphosphate, various materials derived from DOP (9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide) such as DOP-hydroquinone (10-(2',5'-dihydroxyphenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide), condensation products of DOP with glycidylether derivatives of novolacs, and inorganic flame retardants such as aluminum trihydrate, aluminum hydroxide (Boehmite) and aluminum phosphinite.

Mixtures of one or more of the above described flame retardants can also be used.

In one or more embodiments, the curable composition can also include fillers. Examples of fillers include but are not limited to silica, aluminum trihydrate (ATH), magnesium hydroxide, carbon black, and combinations thereof.

The filler is generally present in the curable composition in an amount in the range of from 0.01 weight percent to 50 weight percent, based on the total weight of the curable composition. In another embodiment, the filler is present in an amount in

the range of from 1 weight percent to 50 weight percent, and is present in an amount in the range of from 1 weight percent to 30 weight percent in yet another embodiment.

In one or more embodiments, the curable composition can contain a solvent. Examples of solvents that can be used include, but are not limited to methyl ethyl ketone (MEK), dimethylformamide (DMF), ethyl alcohol (EtOH), propylene glycol methyl ether (PM), propylene glycol methyl ether acetate (DOWANOLTM PMA) and mixtures thereof.

The solvent can generally be present in the curable composition in an amount in the range of from 0 weight percent to 70 weight percent, based on the total weight of the curable composition. In another embodiment, the solvent is present in an amount in the range of from 1 weight percent to 50 weight percent, and is present in an amount in the range of from 30 weight percent to 50 weight percent in yet another embodiment.

15 Process for Producing the Composition

The composition can be produced by any suitable process known to those skilled in the art. In an embodiment, solutions of epoxy resin, hardener and multifunctional vinyl resins are mixed together. Any other desired component, such as the optional components described above, are then added to the mixture.

20 In various embodiments, the composition is cured via a dual curing system to form an interpenetrating polymer network. The curing process can influence the performance of the curable composition and the laminate made from the curable composition. The curing method and temperature can influence the glass transition temperature and dissipation factor. In various embodiments, the curable composition is cured in one step. In various embodiments, the curing temperature is in the range of from 80°C to 300°C, and is in the range of from 150°C to 280°C in various other embodiments. In various embodiments, the curing time is in the range of from 0.5 hours to 24 hours. Upon curing, at least one interpenetrating polymer network system is formed. In an embodiment, an interpenetrating polymer network is formed between 30 the epoxy component and the hardener component. In another embodiment, an

interpenetrating polymer network system is formed between vinyl groups in the vinyl component.

In yet another embodiment, a first interpenetrating polymer network system is formed between the epoxy component and the hardener component and a second
5 interpenetrating polymer network system is formed between vinyl groups in the vinyl component upon curing. In various embodiments, the final product performance can be balanced by controlling the weight ratio between two IPN networks' (the vinyl component network and the epoxy + hardener network).

Embodiments of the present disclosure provide preregs that includes a
10 reinforcement component and the curable composition, as discussed herein. The prepreg can be obtained by a process that includes impregnating a matrix component into the reinforcement component. The matrix component surrounds and/or supports the reinforcement component. The disclosed curable compositions can be used for the matrix component. The matrix component and the reinforcement component of
15 the prepreg provide a synergism. This synergism provides that the preregs and/or products obtained by curing the preregs have mechanical and/or physical properties that are unattainable with only the individual components. The preregs can be used to make electrical laminates for printed circuit boards.

The reinforcement component can be a fiber. Examples of fibers include, but
20 are not limited to, glass, aramid, carbon, polyester, polyethylene, quartz, metal, ceramic, biomass, and combinations thereof. The fibers can be coated. An example of a fiber coating includes, but is not limited to, boron.

Examples of glass fibers include, but are not limited to, A-glass fibers, E-glass fibers, C-glass fibers, R-glass fibers, S-glass fibers, T-glass fibers, and combinations
25 thereof. Aramids are organic polymers, examples of which include, but are not limited to, Kevlar®, Twaron®, and combinations thereof. Examples of carbon fibers include, but are not limited to, those fibers formed from polyacrylonitrile, pitch, rayon, cellulose, and combinations thereof. Examples of metal fibers include, but are not limited to, stainless steel, chromium, nickel, platinum, titanium, copper,
30 aluminum, beryllium, tungsten, and combinations thereof. Examples of ceramic fibers include, but are not limited to, those fibers formed from aluminum oxide,

silicon dioxide, zirconium dioxide, silicon nitride, silicon carbide, boron carbide, boron nitride, silicon boride, and combinations thereof. Examples of biomass fibers include, but are not limited to, those fibers formed from wood, non-wood, and combinations thereof.

5 The reinforcement component can be a fabric. The fabric can be formed from the fiber, as discussed herein. Examples of fabrics include, but are not limited to, stitched fabrics, woven fabrics, and combinations thereof. The fabric can be unidirectional, multiaxial, and combinations thereof. The reinforcement component can be a combination of the fiber and the fabric.

10 The prepreg is obtainable by impregnating the matrix component into the reinforcement component. Impregnating the matrix component into the reinforcement component may be accomplished by a variety of processes. The prepreg can be formed by contacting the reinforcement component and the matrix component via rolling, dipping, spraying, or other such procedures. After the prepreg reinforcement component has been contacted with the prepreg matrix component, the solvent can be removed via volatilization. While and/or after the solvent is volatilized the prepreg matrix component can be cured, e.g. partially cured. This volatilization of the solvent and/or the partial curing can be referred to as B-staging. The B-staged product can be referred to as the prepreg.

20 For some applications, B-staging can occur via an exposure to a temperature of 60 °C to 250 °C; for example B-staging can occur via an exposure to a temperature from 65 °C to 240 °C, or 70 °C to 230 °C. For some applications, B-staging can occur for a period of time of 1 minute (min) to 60 min; for example B-staging can occur for a period of time from, 2 min to 50 min, or 5 min to 40 min. However, for some applications the B-staging can occur at another temperature and/or another period of time.

25 One or more of the prepreps may be cured (e.g. more fully cured) to obtain a cured product. The prepreps can be layered and/or formed into a shape before being cured further. For some applications (e.g. when an electrical laminate is being produced) layers of the prepreg can be alternated with layers of a conductive material. An example of the conductive material includes, but is not limited to, copper foil.

The prepreg layers can then be exposed to conditions so that the matrix component becomes more fully cured.

One example of a process for obtaining the more fully cured product is pressing. One or more prepreps may be placed into a press where it subjected to a curing force for a predetermined curing time interval to obtain the more fully cured product. The press has a curing temperature in the curing temperature ranges stated above. For one or more embodiments, the press has a curing temperature that is ramped from a lower curing temperature to a higher curing temperature over a ramp time interval.

During the pressing, the one or more prepreps can be subjected to a curing force via the press. The curing force may have a value that is 10 kilopascals (kPa) to 350 kPa; for example the curing force may have a value that is 20 kPa to 300 kPa, or 30 kPa to 275 kPa. The predetermined curing time interval may have a value that is 5 s to 500 s; for example the predetermined curing time interval may have a value that is 25 s to 540 s, or 45 s to 520 s. For other processes for obtaining the cured product other curing temperatures, curing force values, and/or predetermined curing time intervals are possible. Additionally, the process may be repeated to further cure the prepreg and obtain the cured product.

The prepreps can be used to make composites, electrical laminates, and coatings.

EXAMPLES

Ingredients

DERTM 560 resin (diglycidyl ether of tetra- bromobisphenol A) from Dow Chemical Company

DENTM 438EK85 resin (85% epoxy novolac in MEK) from Dow Chemical Company

TBBA (tetrabromobisphenol A) from Albemarle Corporation

Ricobond[®] 1756 (liquid polybutadiene co-maleic anhydride) from

Cray Valley

SMA[®] EF 40 (styrene maleic anhydride copolymer, styrene: maleic anhydride (mole ratio)=4:1) from Cray Valley

5 MX9000 (vinyl capped polyphenylene ether oligomer (Mn is about 1600)) from SABIC

TAIC (1,3,5-triallyl isocyanurate) from Tokyo Chemical Industry Co. LTD

VTBBA (vinyl capped TBBA) synthesized from TBBA and vinyl benzyl chloride

10 VNPN (vinyl capped naphthol novolac) synthesized from the naphthol novolac and vinyl benzyl chloride

2-MI (2-methylimidazole) from Aldrich

2-PI (2-phenylimidazole) from Aldrich

2E-4MI (2-ethyl-4-methyl imidazole) from Aldrich

15 DCP(dicumyl peroxide) from Sinopharm Chemical Reagent Co.Ltd

Examples

Part A

In Part A, one network formed via a free radical curing reaction with vinyl capped PPO and another network formed via a curing reaction between an epoxy and an epoxy hardener. 30 grams of MX9000 powder was dissolved in 30 grams of MEK to yield a MX9000-MEK solution (50%). 30.5 grams DER[™] 560 solid resin was dissolved in 30.5 grams of MEK to get the DER[™] 560 solution (50%). 29.5 grams of SMA[®] EF 40 solid resin was dissolved in 29.5 grams of MEK to yield a SMA[®] EF 40 solution (50%). The above three solutions were mixed together and an appropriate amount of 10% 2-methylimidazole solution as a catalyst was added and a uniform solution was obtained. Comparative examples A and B and Example 1 were prepared according to the formulations listed in Table 1. The resin formulation was brushed on woven glass fabrics and partially cured to prepare prepregs. The prepregs were twisted and a partially cured resin powder was obtained. The resin powder was molded at 195°C for 1 hour in a hot press machine for testing the dielectric properties

and thermal properties. In order to test the copper adhesion strength, the laminates were prepared with using 8 pieces of the above prepregs with the 1 oz copper clad and molded at 195°C for 1 hour.

5 Part B

In Part B, covalent bonds formed between two networks. A free radical curing reaction occurred between vinyl groups in LPBMA (liquid polybutadiene co-maleic anhydride) and vinyl groups in PPO. 5.2 grams of a DENTM 438-EK85 solution, 11.0 grams DERTM 560 solid epoxy resin and 5.7 grams MEK as a solvent were mixed
10 together to yield a uniform solution. 17.4 grams of Ricon[®] 1756 with high viscosity was dissolved in 17.4 grams of xylene to yield a Ricon[®] 1756-xylene solution (50%). 24 grams of MX9000 powder was dissolved in 24 grams of MEK to yield a MX9000-MEK solution (50%). The above three solutions were then mixed together. Appropriate amounts of TBBA powder, DCP as a radical curing initiator and 2-
15 phenylimidazole (or 2-ethyl-4-methylimidazole) solution as a catalyst were then added to the solution. Comparative examples C, D and E and Examples 2 and 3 were prepared according to the formulations listed in Table 2. The resin formulation was poured onto a flat plate which was coated with a releasing agent. After the solvent was removed in a vacuum oven, samples were cured at 200°C for 2 hours and the
20 properties of the casted samples were tested. The samples were then post cured at 250°C for another 2 hours and the properties of the post cured cast samples were tested. For the copper peel strength testing, laminates were prepared with 8 sheets of the prepregs and 1 oz copper foil using the above formulations and was molded at 200°C for 2 hours and 250°C for 2 hours.

25

Part C

Synthesis of VTBBA:

A reactor equipped with a stirrer, a thermometer, a reflux tube and a tube for the introduction of gases under nitrogen flow was charged with 32.64 grams of
30 TBBA, 21.37 grams of vinyl benzyl chloride (from Sinopharm Chemical Reagent Co.,Ltd), 17.39 grams of K₂CO₃, 0.5 grams of KI, 0.8 grams of 18-crown-6 ether and

300 ml acetone and the components were stirred at a reaction temperature of 60°C. The reaction was terminated after 20 hours of stirring and the residual solid in the solution was removed. The VTBBA solution was added drop-wise into methanol. The precipitated resin was filtered and dried in the vacuum oven at 50 °C for 3 hours. 40.5 grams of a white solid was obtained.

A free radical curing reaction occurred between vinyl groups in LPBMA (liquid polybutadiene co-maleic anhydride) and vinyl groups in VTBBA. 5.2 grams of DENTM 438-EK85 solution, 11.0 grams of DERTM 560 solid epoxy resin and 5.7 grams of MEK as a solvent were mixed together to yield a uniform solution. 25.8 grams of Ricon[®] 1756 with high viscosity was dissolved in 25.84 grams of xylene to get the Ricon[®] 1756-xylene solution (50%). 14 grams of the VTBBA white powder was dissolved in 14 grams of MEK to yield a VTBBA-MEK solution (50%). The above three solutions were mixed together. DCP as a radical curing initiator and 2-phenylimidazole (or 2-ethyl-4-methylimidazole) solution as a catalyst were both added to the solution. The VTBBA in the formulation was both the flame retardant and crosslinker. Example 4 was prepared according to the formulations listed in Table 3. The resin formulation was poured onto a flat plate which was coated with the releasing agent. After the solvent was removed in a vacuum oven, samples were cured at 200°C for 2 hours and the properties of the casted samples were tested. Afterwards, the samples were post cured at 250°C for another 2 hours and the properties of the post cured cast samples were tested.

Part D

Synthesis of VNPN in two steps:

First step: NPN synthesis

In a 1000 ml three-necked reactor equipped with a refluxing condenser, a nitrogen inlet and temperature sensor, 72 grams of 1-naphthol (0.5 mole) was added to 500 ml of toluene. The mixture was heated to 50 °C to dissolve the 1-naphthol in the solvent. 13 grams of paraformaldehyde (0.5 * 0.87 mol) and 1.26 grams of oxalic acid (0.5 * 0.02 mol) were added. The reaction was heated to 70 °C and temperature automatically rose to 75-80 °C in 10 minutes and then dropped to 70 °C. The toluene

mixture was heated to reflux and stirred under nitrogen for 48 hours. The reaction mixture was then allowed to cool to 50 °C and the products precipitated from the solution. The upper toluene solution was poured out and 200 ml of ethyl acetate was added and stirred for additional 10 minutes. The ethyl acetate solution was washed by water three times and organic phase was collected and dried over anhydrous sodium sulfate for 2 hours. The solid was filtered and most of the solvent was removed under vacuum.

Second step: VNPN synthesis

10 A reactor equipped with a stirrer, a thermometer, a reflux tube and a tube for the introduction of gases under nitrogen flow was charged with 30 grams of NPN, 36.96 grams of vinyl benzyl chloride, 30.09 grams of K₂CO₃, 1.5 grams of KI, 1.5 grams of 18-crown-6 ether and 450 ml of acetone and the components were stirred at a reaction temperature of 60 °C. The reaction was terminated after 20 hours and the solid in the solution was removed. The product VNPN was obtained from the solution after purifying by re-precipitation with methanol. 27.3 grams of a brown solid was obtained after drying in the vacuum oven at 50 °C for 3 hours.

A free radical curing reaction occurred between vinyl groups in LPBMA (liquid polybutadiene co-maleic anhydride) and vinyl groups in VNPN. 5.2 grams of DENTM 438-EK85 solution, 11.0 grams of DERTM 560 solid epoxy resin and 5.7 grams of MEK as a solvent were mixed together to yield a uniform solution. 18.0 grams of Ricon[®] 1756 was dissolved in 18.0 grams of xylene to get the Ricon 1756-xylene solution (50%). 24.7 grams of VNPN powder was dissolved in 24.7 grams of MEK to yield a VNPN-MEK solution (50%). The above three solutions were mixed together. TBBA powder as a flame retardant agent, DCP as radical curing initiator and 2-phenylimidazole (or 2-ethyl-4-methylimidazole) solution as a catalyst were all added to the solution. Example 5 was prepared according to the formulations listed in Table 3. The resin formulation was poured onto a flat plate which was coated with a releasing agent. After the solvent was removed in a vacuum oven, samples were cured at 200°C for 2 hours and the properties of the casted samples were tested.

Afterwards, the samples were post cured at 250°C for another 2 hours and the properties of the post cured cast samples were tested.

The formulations, thermal performance (Tg and Td), electrical and adhesion properties are shown in Tables 1, 2 and 3. All the data were tested on the clear cast
5 plaques, except for the copper peel strength data obtained from the copper foil laminates.

Table 1 Formulation and electrical properties and thermal performance of SMA based dual cure resin

Components	Comp Ex A (solid wt/g)	Comp Ex B (solid wt/g)	Example 1 (solid wt/g)
DER TM 560	15.3	0	15.3
SMA [®] EF 40	14.8	0	14.8
MX9000	0	15	15
2-MI	0.0122	0	0
Bake condition	195 °C -1h	195° C -1h	195 °C -1h
Tg / °C	166 (DMA)	164 (DSC)	172 (DMA)
Td / °C (5% Loss)	354	427	355
Dk / 1GHz	3.02	2.66	2.87
Df / 1GHz	0.011	0.002	0.006
Peel Strength / Lb·in ⁻¹	4.0827	0.2372	0.9184

Table 2 Formulation and electrical properties and thermal performance of LPBMA based dual cure resin

Components	Comp Ex C (solid wt/g)	Comp Ex D (solid wt/g)	Comp Ex E (solid wt/g)	Example 2 (solid wt/g)	Example 3 (solid wt/g)
DER TM 560	11.0	0	0	11.0	11.0
DEN438-EK85	5.2	0	0	5.2	5.2
Ricon [®] 1756	17.4	0	0	17.4	17.4
TBBA	3.85	0	0	3.85	3.85
MX9000	0	10	10	24	0
TAIC	0	0	0	0	5
DCP	1.39	0	0.4	1.39	1.39
2-PI	0.0150	0	0	0.0150	0
2E-4MI	0	0	0	0	0.0070
Bake condition	200°C -2h	200°C -2h	200°C -2h	200°C -2h	200°C -2h
Tg / °C (DMA)	115	165 (DSC)	214 (DSC)	152	105(T _{g1})/181(T _{g2})
Dk / 1GHz	2.71	2.70	NA	2.75	2.78
Df / 1GHz	0.008	0.002	NA	0.007	0.006
Bake condition	200°C -2h & 250°C -2h	200°C -2h & 250°C -2h	200°C -2h & 250°C -2h	200°C -2h & 250°C -2h	200°C -2h & 250°C -2h
Tg / °C (DMA)	140	181 (DSC)	238 (DSC)	185	162
Td / °C (5% Loss)	360	428	NA	364	368
Dk / 1GHz	2.69	2.68	NA	2.61	2.72
Df / 1GHz	0.007	0.002	NA	0.006	0.007
Peel Strength / Lb·in ⁻¹	7.056	NA	NA	6.488	6.1205

Table 3 Formulation and electrical properties and thermal performance of LPBMA/new vinyl materials based dual cure resin

Components	Example 4 (solid wt/g)	Example 5 (solid wt/g)
DER TM 560	11.0	11.0
DEN438-EK85	5.2	5.2
Ricon [®] 1756	25.8	18.0
TBBA	0	3.67
VTBBA	14.0	0
VNPN	0	24.7
DCP	1.59	1.71
2-PI	0.017	0.016
Bake condition	200 °C -2h	200 °C -2h
T _g / °C (DMA)	119	133
Dk / 1GHz	2.88	2.82
Df / 1GHz	0.015	0.009
Bake condition	200°C -2h & 250°C -2h	200°C -2h & 250°C -2h
T _g / °C (DMA)	174	171
T _d / °C (5% Loss)	346	342
Dk / 1GHz	2.80	2.93
Df / 1GHz	0.009	0.009

5 Test Methods

Glass Transition Temperature (T_g)

Glass transition temperature was determined by Differential Scanning Calorimetry (DSC) using a Q2000 machine from TA Instruments. Typically, a thermal scan ranges from room temperature to 250 °C and heating rate of 10 °C/min was used. Two heating cycles were performed, with the curve from the second cycle used for T_g determination by “middle of inflection” method.

Alternatively, the glass transition temperature was determined from tangent delta peak on a RSA III dynamic mechanical thermal analyzer (DMTA). Samples were heated from 20 °C to 250 °C at a heating rate of 3 °C/min. Test frequency was 6.28 rad/s.

Thermal Decomposition Temperature (Td)

The cured resin was evaluated on a Q50 machine from TA Instruments. The heating rate was 10 °C/min. The Td is defined as temperature at 5% weight loss.

5 Dielectric Constant (D_k)/Dissipation Factor (D_f)

An epoxy plaque was made for dielectric measurement. Prepreg powder was placed into two aluminum foils. The assembly was hot pressed at required conditions in the Table 1 to 3. An air bubble-free epoxy plaque with a thickness between 0.5 and 0.8 mm was obtained.

10 The dielectric constant and dissipation factor were determined by an Agilent E4991A RF Impedance/Material Analyzer equipped with Agilent 16453A test fixture under 1 GHz at 24 °C following ASTM D-150.

Copper Peel Strength (CPS)

15 Copper peel strength was measured using an IMASS SP-2000 slip/peel tester equipped with a variable angle peel fixture capable of maintaining the desired 90° peel angle throughout the test. For the copper etching, 2"x4" copper clad laminates were cut. Two strips of ¼" graphite tape were placed lengthwise along the sample on both faces of the laminate with at least a ½" space between them. The laminate pieces
20 were then placed in a KeyPro bench top etcher. Once the samples were removed from the etcher and properly dried, the graphite tape was removed to reveal the copper strips. A razor blade was used to pull up ½ of each copper strip. The laminate was then loaded onto the IMASS tester. The copper strip was clamped and the copper peel test was conducted at a 90° angle with a pull rate of 2.8 in/min.

25

WHAT IS CLAIMED IS:

1. A curable composition comprising
 - a) an epoxy component;
 - b) a hardener component selected from the group consisting of a
5 maleic anhydride-containing compound, a maleic anhydride-containing vinyl
compound, and combinations thereof; and
 - c) a vinyl componentwherein upon curing under curing conditions, the curable composition forms at least one interpenetrating polymer network.
- 10 2. A curable composition in accordance with claim 1 wherein the epoxy component is selected from the group consisting of a multifunctional epoxy resin, a flame retardant epoxy resin, and combinations thereof.
3. A curable composition in accordance with claims 1 or 2 further comprising a free radical initiator selected from the group consisting of 2,2'-
15 azobisisobutylnitrile, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, benzoyl peroxide, dicumyl peroxide, a disulfide, and combinations thereof.
4. A curable composition in accordance with claims 2 or 3 wherein the multifunctional epoxy is present in the range of from 0 weight percent to 60 weight percent, based on the total weight of the epoxy component.
- 20 5. A curable composition in accordance with any one of the preceding claims further comprising a catalyst selected from the group consisting of 2-methylimidazole, 2-phenyl imidazole, 2-ethyl-4-methyl imidazole, boric acid, triphenylphosphine, tetraphenylphosphonium-tetraphenylborate and mixtures thereof.
6. A curable composition in accordance with any one of the preceding
25 claims wherein the vinyl component is selected from the group consisting of vinyl capped poly(phenylene) ether, 1,3,5-triallyl isocyanurate, divinylbenzene, dicyclopentadiene, vinyl capped tetrabromobisphenol A, vinyl capped bisphenol A, vinyl capped phenol novolac, vinyl capped naphthol novolac, bismaleimide, maleated rosin, and combinations thereof.
- 30 7. A curable composition in accordance with claim 6 wherein the vinyl component further comprises epoxide-reactive groups and vinyl groups.

8. A curable composition in accordance with claim 7 wherein the epoxide-reactive groups are selected from the group consisting of anhydride groups, hydroxyl groups, and combinations thereof.

5 9. A curable composition in accordance with any one of the preceding claims wherein the hardener is selected from the group consisting of polybutadiene co-maleic anhydride, styrene-maleic anhydride, maleinized polybutadiene styrene copolymer, and combinations thereof.

10 10. A curable composition in accordance with any one of the preceding claims wherein the epoxy component and the hardener component are together present in an amount in the range of from 0.1 weight percent to 50 weight percent and the vinyl component is present in an amount in the range of from 0.1 weight percent to 50 weight percent, based on the total weight of the curable composition.

15 11. A curable composition in accordance with any one of claims 2-10 wherein the free radical initiator is present in an amount in the range of from 0.01 weight percent to 10 weight percent, based on the total weight of the curable composition.

12. A curable composition in accordance with any one of the preceding claims wherein the curing conditions comprise a curing temperature of from 80°C to 300°C.

20 13. A curable composition in accordance with any one of the preceding claims wherein upon curing under curing conditions, an interpenetrating polymer network system is formed between the epoxy component and the hardener component.

25 14. A curable composition in accordance with any one of the preceding claims wherein upon curing under curing conditions, an interpenetrating polymer network system is formed between vinyl groups in the vinyl component.

30 15. A curable composition in accordance with any one of the preceding claims wherein upon curing under curing conditions, a first interpenetrating polymer network system is formed between the epoxy component and the hardener component and a second interpenetrating polymer network system is formed between vinyl groups in the vinyl component.

16. A process comprising
- a) admixing
- i) an epoxy component;
- ii) a hardener component selected from the group consisting of
- 5 polybutadiene co-maleic anhydride, styrene-maleic anhydride, maleinized polybutadiene styrene copolymer, and combinations thereof; and
- iii) a vinyl component
- to form a curable composition; and
- b) curing the curable composition under curing conditions to form a
- 10 cured product having an interpenetrating polymer network.
17. A process in accordance with claim 16 wherein the epoxy component is selected from the group consisting of a multifunctional epoxy resin, a flame retardant epoxy resin, and combinations thereof.
18. A process in accordance with any one of claims 16 or 17 wherein the
- 15 vinyl component is selected from the group consisting of vinyl capped poly(phenylene ether), 1,3,5-triallyl isocyanurate, divinylbenzene, dicyclopentadiene, vinyl capped tetrabromobisphenol A, vinyl capped naphthol novolac, bismaleimide, maleated rosin, and mixtures thereof.
19. A process in accordance with any one of claims 16-18 further
- 20 comprising admixing in step a) a free radical initiator selected from the group consisting of 2,2'-azobisisobutyronitrile, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, benzoyl peroxide, dicumyl peroxide, a disulfide, and combinations thereof.
20. A process in accordance with any one of claims 16-19 wherein the
- epoxy component and the hardener component are together present in the curable
- 25 composition in an amount in the range of from 0.1 weight percent to 50 weight percent and the vinyl component is present in an amount in the range of from 0.1 weight percent to 50 weight percent, based on the total weight of the curable composition.
21. A process in accordance with any one of claims 16-20 wherein the free
- 30 radical initiator is present in the curable composition in an amount in the range of

from 0.01 weight percent to 10 weight percent, based on the total weight of the curable composition.

22. A process in accordance with any one of claims 16-21 wherein the curing conditions comprise a curing temperature of from 80°C to 300°C.

5 23. A process in accordance with any one of claims 16-22 wherein an interpenetrating polymer network system is formed between the epoxy component and the hardener component after the curing in step b).

10 24. A process in accordance with any one of claims 16-23 wherein an interpenetrating polymer network system is formed between vinyl groups in the vinyl component after the curing in step b).

15 25. A process in accordance with claim 24 wherein upon curing under curing conditions, a first interpenetrating polymer network system is formed between the epoxy component and the hardener component and a second interpenetrating polymer network system is formed between vinyl groups in the vinyl component after the curing in step b).

26. A prepreg prepared from the curable composition of claim 1.

27. An electrical laminate prepared from the curable composition of claim 1.

20 28. A printed circuit board prepared from the curable composition of claim 1.

25

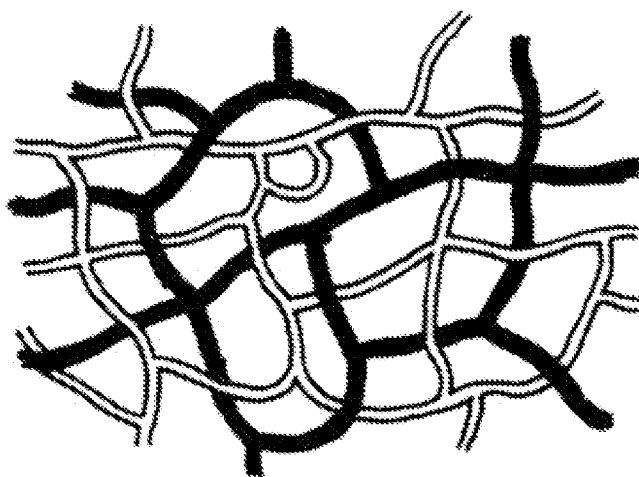


FIGURE 1

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/062615

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G59/42 C08J5/24
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 106 924 A (SMITH JAMES D B [US] ET AL) 21 April 1992 (1992-04-21) claims 1-13 column 6, lines 39-54 examples 1-2 -----	1,2,4, 10, 13-17, 20,24-28
X	WO 99/10405 A1 (RANBAR ELECTRICAL MATERIALS IN [US]) 4 March 1999 (1999-03-04) claims 1-31 page 26, lines 1-6 examples 1-7 ----- -/-	1,2,4, 10, 12-17, 20,22-25



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

22 January 2015

Date of mailing of the international search report

28/01/2015

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Mensah, Laure

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/062615

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/224332 A1 (HE YUFANG [CN] ET AL) 15 September 2011 (2011-09-15) claims 1, 11 page 2, paragraph 12 page 3, paragraph 23 -----	1,2,4-6, 9,10, 12-18, 20,22-28
X	US 3 919 348 A (FOSTER NEWTON C ET AL) 11 November 1975 (1975-11-11) claims 1-15 examples 1-4 column 12, lines 21-25 column 11, lines 38-44 -----	1-28
E	US 2014/378580 A1 (AMOU SATORU [JP]) 25 December 2014 (2014-12-25) the whole document -----	1,2,4, 10, 12-17, 20,22-25

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/062615

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5106924	A	21-04-1992	CA 2035636 A1 06-08-1991
			JP 2907351 B2 21-06-1999
			JP H04218556 A 10-08-1992
			US 5106924 A 21-04-1992

WO 9910405	A1	04-03-1999	AU 744290 B2 21-02-2002
			AU 9293798 A 16-03-1999
			BR 9806149 A 31-10-2000
			CA 2269785 A1 04-03-1999
			EP 0935629 A1 18-08-1999
			JP 2001504894 A 10-04-2001
			US 6127490 A 03-10-2000
			WO 9910405 A1 04-03-1999
			ZA 9807756 A 13-05-1999

US 2011224332	A1	15-09-2011	NONE

US 3919348	A	11-11-1975	FR 2272141 A1 19-12-1975
			JP S51594 A 06-01-1976
			JP S5344198 B2 27-11-1978
			US 3919348 A 11-11-1975

US 2014378580	A1	25-12-2014	CN 104093763 A 08-10-2014
			JP 2013256637 A 26-12-2013
			KR 20140119075 A 08-10-2014
			US 2014378580 A1 25-12-2014
			WO 2013172064 A1 21-11-2013
